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Recoverable-Mercury Sorbents

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13. ABSTRACT (<i>Maximum 200 words</i>) An inexpensive material was recently developed that appears to effectively capture mercury from simulated coal-fired flue gases when injected into ductwork at modest rates. Importantly, the new sorbents appear to be effective at high temperatures, 300°F to 400°F. This means that inexpensive gas-cooling or fabric-filter retrofits are not required and that fly ash will remain saleable. Consequently, preliminary estimates of their cost effectiveness suggest costs approximately one-tenth of those estimated by the EPA for other technologies.		
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INTRODUCTION

The emission of mercury from combustion sources into the atmosphere has increasingly become a major environmental and health concern.^{1,2} Because of their low vaporization points, mercury species liberated during combustion, incineration, or smelting processes largely escape traditional air pollution controls and are released into the air. The mercury vapor can then travel long distances before being deposited in soil and water. It is usually chemically altered in the environment and becomes biologically concentrated as it moves up through the food chain toward humans.

Recognizing its dangers, the 1990 Clean Air Act Amendments have called for tightened mercury emission guidelines for incinerators and studies on mercury emissions from coal-fired boilers.³

Because mercury species in exhaust gases are typically in dilute, parts-per-billion concentrations, their selective removal is difficult and expensive. To further complicate the control and measurement of mercury, it can exist in gas streams as different species, primarily as elemental mercury (Hg^0) and mercury chloride (in mercury's oxidized form, Hg^{+2}).⁴ The elemental form of mercury, in particular, has proven especially difficult to control.^{5,6}

Those looking for highly efficient control technology for mercury have few alternatives. Existing air pollution control systems, such as wet scrubbers, spray dryers, electrostatic precipitators, and fabric filters have shown highly variable and generally poor results in reducing mercury emissions from different sources.⁷

Activated carbons, sometimes chemically impregnated, have shown an affinity for mercury removal. Fixed beds of granular carbon have been used to remove mercury vapors from small gas volumes in chloro-alkali plants and other industrial processes in the past.⁸ The co-absorption of water and SO_2 , leading to bed-soaking and corrosive sulfuric acid production, however, has limited this method of control. Moreover, activated carbon beds can spontaneously combust. Activated carbons can also be injected into the gas stream and removed in a particulate removal device.⁹ However, these carbons can be expensive and high injection rates may be necessary to get a high elemental mercury removal. Moreover, once carbons are injected, they are lost; they become mixed in with large masses of HCl^- or SO_2 -sorbents and/or fly ash, which go to disposal and any sorbed mercury is not recovered, but left to be a potential solid waste or water pollution problem.

An effort, sponsored by the U.S. EPA and the Air Force, is being conducted at Sorbent Technologies Corporation to develop a new low-cost, high-effectively recoverable-mercury sorbent. The initial effort focuses on waste incinerator streams, although application on coal-fired utility streams will be examined if appropriate. While mercury chloride is also a major specie of concern, the initial effort concentrates on elemental mercury. This paper presents early laboratory and bench-scale results.

EXPERIMENTAL APPROACH

A laboratory-scale, fixed-bed test stand was constructed to evaluate the performance of various elemental mercury sorbent chemistries. A schematic diagram of the stand is presented in Figure 1. The test stand consisted of bottled gases, mass flow controllers, a constant-temperature oil bath, laboratory oven, mercury analyzer, and a computer data acquisition system.

The exhaust gas of a waste incinerator was simulated in these experiments. Elemental mercury was introduced into the simulation gas from permeation tubes supplied by VICI Metronics. These tubes emit highly-constant elemental mercury vapor at rates strictly dependent on their temperature. A certified permeation tube, traceable to NIST standards, was used to calibrate the analyzer. During testing, the permeation tubes were placed inside a glass container that was maintained at a constant temperature using a constant-temperature oil bath. The permeation rate of mercury was varied by using multiple permeation tubes or by changing the temperature of the bath. For screening purposes, the mercury spiking concentrations were chosen higher than is normally seen in practice in order to make measurement easier and to enable early observation of any sorbent saturations. The simulated conditions were closer to those of incinerators than to power plants, where mercury concentrations are significantly lower, but gas volumes are higher.

Mass-flow controllers were used to obtain the desired concentrations of the component gases at the desired flow rates. All or part of the total gas flow was passed through the glass tube holder to convey the permeated mercury vapors through the sorbent bed. To prevent the absorption of mercury by the test apparatus, all components exposed to the mercury-laden gas stream were constructed of Teflon or glass. To test the various materials, a small fixed-bed of sorbent material was held in a custom-fabricated glass chamber which was heated in a double-wall laboratory oven to the simulation temperature. The mercury-laden gas was combined with make-up gas and pre-heated in a glass-bead loaded preheater before it entered the sorbent bed. A data acquisition system allowed long-term, unattended system operation.

The mercury measurements were made using a Jerome 431-X gold-film mercury analyzer manufactured by Arizona Instruments. This instrument has also been used by other researchers.^{10,11} The Jerome analyzer uses a gold-film sensor for the measurement of elemental mercury vapor. The gold-film sensor is inherently stable, selective to elemental mercury, and has a detection range from 0 to 999 $\mu\text{g}/\text{Nm}^3$. The sensor is periodically regenerated.

RESULTS

Mercury Sorption Tests

A large series of sorbent screening runs were conducted on the laboratory test stand. Exfoliated vermiculites were given various chemical pretreatments and tested for their elemental mercury sorption capabilities. Vermiculite is a high-surface-area industrial mineral that was used as a granular support medium for the tested chemistries. While the majority of treatments gave little evidence of mercury sorption, a few showed remarkable performance. One chemical combination, in particular, showed especially promising mercury-capture abilities.

The new sorbent's potential for long-term elemental mercury-capture is suggested in Figure 2. With a mercury inlet concentration of 150 $\mu\text{g}/\text{Nm}^3$, a space velocity of 2400 hr^{-1} , and a 7.6-cm deep sorbent bed, a removal rate of over 95% was obtained with no diminution in performance in a 70-hour run. The ultimate capacity of the sorbents has not yet been determined, but it is expected to be many times higher than shown here. The target is a sorbent that would last from six-months to two years.

Testing was also performed to evaluate the effect of operating temperature on the performance of the new sorbent. As shown in the short-term test described in Figure 3, the applicable temperature range

of the sorbents was from about 55 to 115°C. Many exhaust gases are available for treatment in this range, particularly where spray dryers are installed. Work is underway to extend this temperature range to encompass more potential gas streams.

Many mercury-containing gases will also contain SO₂. The performance of activated carbons and zeolites, for example, can be adversely affected by the co-existence of SO₂ in the gas stream. Consequently, the performance of the new sorbent in an SO₂-environment was tested. As revealed in Figure 4, no significant effect of SO₂ on the performance of the new sorbent was observed when the SO₂ concentration was changed from 0 to 500 ppm. Similarly, CO₂ had little to no effect.

Sorption testing was then scaled up to a large 150 m³/hr (90 acfm) simulation system. This system included a propane burner, elemental mercury spiking system, dilution air intake for temperature control, 24 m of ducting, an orifice plate for flow measurement, three heated sample lines for gas analysis at various points, and a variable speed ID fan. The spiking system was capable of adding 50 µg/Nm³ of elemental mercury to the hot gas stream.

A thin filter of the new sorbent was inserted into the end of the ducting. The conically-shaped, flat filter was 1 m high, 0.5 m at its maximum diameter, and 7.5 cm thick. It held 15 kg of the new sorbent. At a gas flow rate of 150 m³/hr, with a space velocity of 2700 hr⁻¹, the pressure drop across the filter was only 0.5 cm of water column. When operated in multi-hour tests, the sorbents removed from 80% to 100% of the mercury passing through them, depending on the operating conditions.

Mercury Desorption Tests

Effectively sorbing the mercury from the exhaust gas is not enough; it must be assured that it no longer threatens human health or the environment. Consequently, leachability and thermal desorption tests were conducted to explore the safety and mercury recovery potential of the new sorbent.

Saturated sorbent containing approximately 0.12 wt% of mercury from a long-term utilization test run was used in these studies.

If a waste material like the saturated sorbents is easily leachable, heightened precautions are necessary in its storage and transport, and disposal can be very expensive. The TCLP mercury leachate level to qualify as hazardous wastes is 0.200 mg Hg/liter. Two 5-gram samples of the partially-saturated sorbent, containing approximately 6,000 µg of mercury, were sent to an independent testing laboratory for standard Toxic Characteristic Leaching Procedure (TCLP) extraction analysis. The TCLP analysis was performed by Electro-Analytical Laboratories of Mentor, Ohio. Consequently, two identical samples were subjected to an 18-hour extraction with a 20:1 solution-to-solids ratio using an acetic acid solution with a pH of 2.9. The detection limit of the process was 0.010 mg Hg/liter. The first sample had a TCLP extraction test result of 0.082 mg Hg/liter; the second sample had a result of 0.080 mg Hg/liter. Thus, these saturated sorbent samples would not be classified as a hazardous waste.

It is not ultimately helpful to remove mercury from the gas phase if it is simply transferred to another medium. Mercury captured by activated carbon injection, for example, becomes mixed in with other fly ash that is ultimately sent out for land disposal. The mercury is not recovered, but left to become a potential groundwater pollutant.¹² The sorbents examined in this research, however, present the possibility of mercury recovery.

Throughout the world, the primary source of elemental mercury is cinnabar ore, or mercury sulfide. A growing secondary source of mercury supply is recovery from mercury-containing wastes, which are roasted in retort furnaces to recycle their mercury. There are now numerous facilities in the U.S. retorting these wastes and condensing out mercury for sale. With the mercury content of the sorbent in at least the same range as the cinnabar ores, it should be possible to have the sorbent mercury reclaimed by such primary or secondary source mercury producers.

Experiments were performed to examine this possibility. The first thermal desorption test was performed on 0.50 g of the saturated sorbent at 230°C. The result is shown in Figure 5. Integration of the area under the desorption curve reveals that about 85% of the absorbed mercury was desorbed as elemental mercury after six hours at this temperature. Desorption was sensitive to even a small temperature increase. A 30°C bump in the temperature desorbed a good deal of additional mercury.

Mercury recovery retort furnaces and ore roasters, however, operate at much higher temperature. A second test was conducted at a temperature of 600°C. At this temperature, mercury desorbed from the materials so quickly and in such quantities that the initial exit mercury concentration was far over the upper detection limit of the analyzer, even with 80:1 dilution sampling. However, this mercury concentration rapidly dropped to zero in a period of two minutes, indicated a very fast desorption process under this temperature. Thus, the mercury captured by the new sorbents should be desorbed very quickly by the retort furnaces at mercury recovery facilities, which operate at around 600°C.

Power Plant Slip-Stream Testing

The new sorbents were also tested in the field on actual flue gas from the Ohio Edison Company's base-loaded R.E. Burger station near Shadyside, Ohio. A test rig was constructed that drew off a slipstream of the plant flue gas after the electrostatic precipitator and divided it between six small test beds. Approximately 550 lpm of gas with approximately 3.5 µg/Nm³ of elemental mercury was drawn through each sorbent test bed, 13-cm in diameter and 15-cm deep for nine days. A blower returned the gas to the ductwork.

Each sampling train consisted of a particulate pre-filter, ice bath, two acid-gas filters in series, two gold-coil dosimeters, a mass flow controller, and a pump operating at 90 cc/min. The acid-gas filters were to eliminate any hydrogen sulfide or other acidic gases. The gold-film dosimeters are made to sorb very low concentrations of elemental mercury, concentrating it for more accurate measurement. Two dosimeters in series were used to insure that all of the elemental mercury was collected. They are not supposed to sorb any mercury chloride that may be in the gas. After 90 minutes, the dosimeters were removed and analyzed using the Jerome instrument. The elemental mercury concentrations of the gas is the mass of mercury collected divided by the total gas volume sampled. To save time, three sampling lines, with a total of six dosimeters, were run simultaneously.

The mercury content of gas from power plants is about two orders of magnitude lower than that of waste incinerators and some measurement difficulties were experienced. An interferant gas appeared to affect our measurements at these levels. By using a plain vermiculite dummy bed, however, a method was developed to correct the readings. Using the dummy-bed correction, the elemental mercury removal rates measured after nine days varied from between about 75% and 97%, similar to what was seen in the laboratory. These numbers are approximate because the mercury sampling at the power plant was episodic and the inlet mercury would be expected to vary over the nine days.

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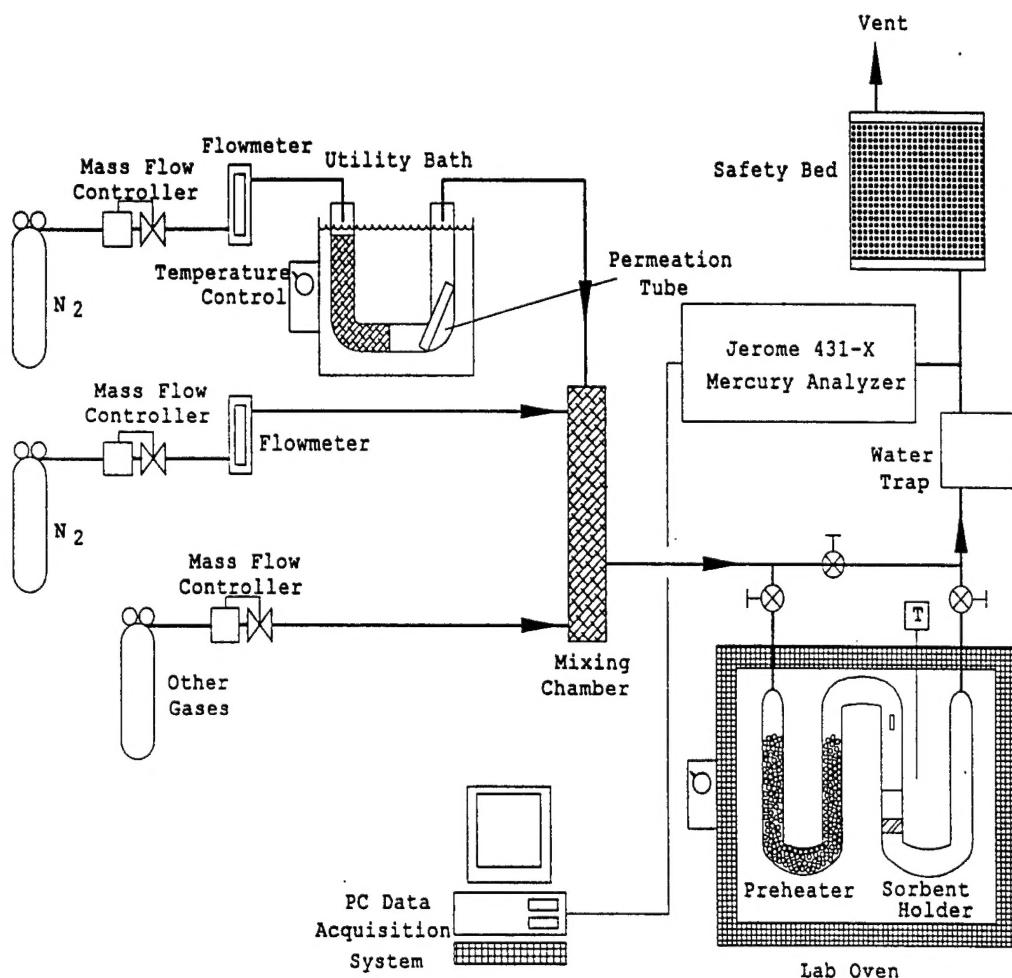


Figure 1. Laboratory elemental mercury sorption test stand.

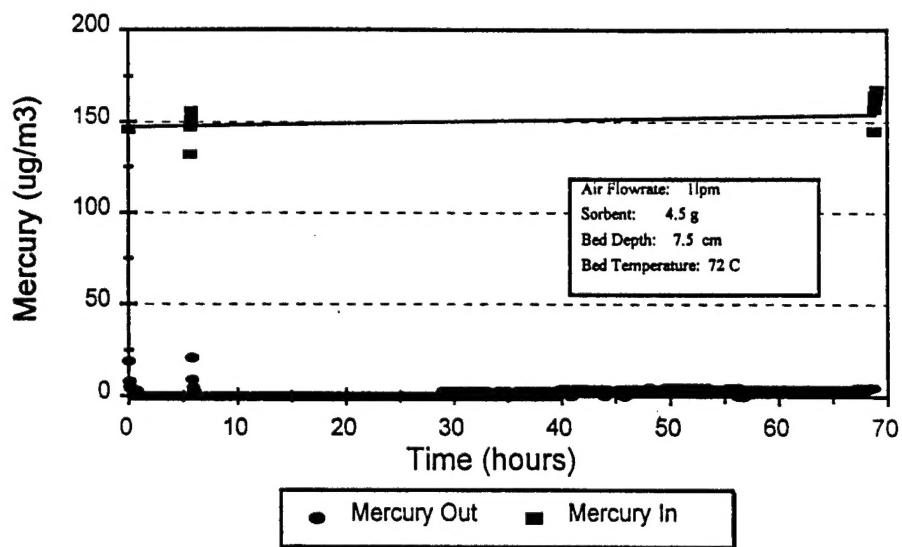


Figure 2. Extended test of elemental mercury sorption performance.

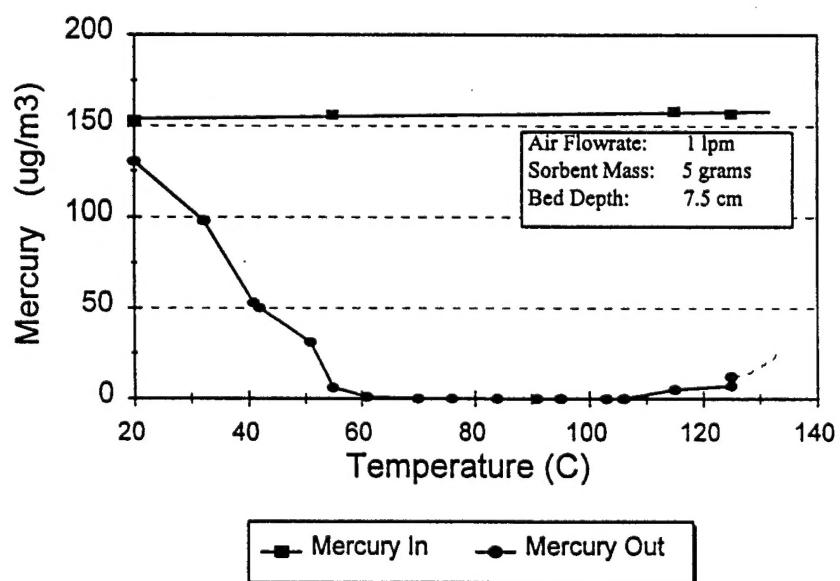


Figure 3. Temperature range of the new sorbent.

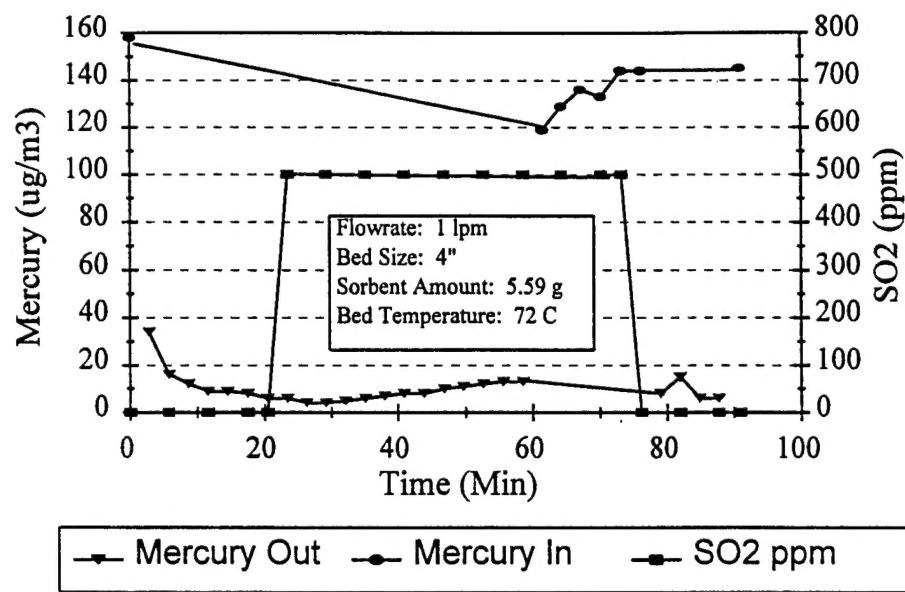


Figure 4. Effect of SO_2 on the performance of the new mercury sorbent.

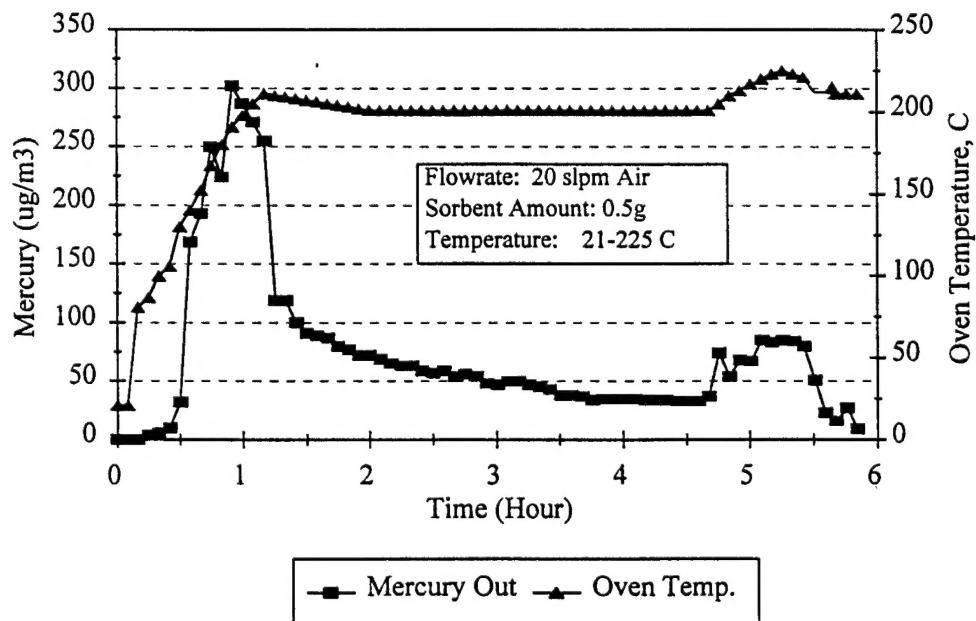


Figure 5. Desorption test on partially-saturated sorbent.

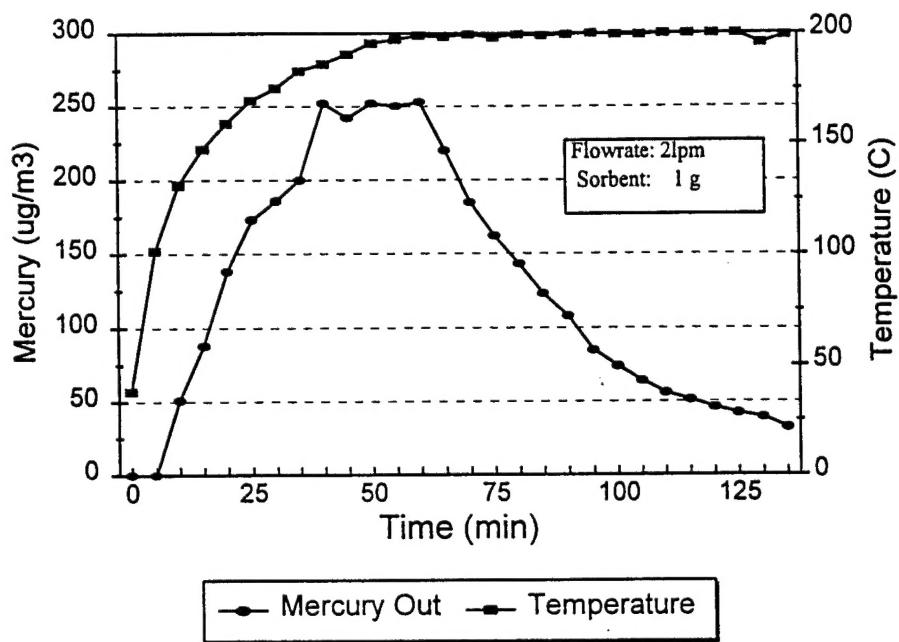


Figure 6. Desorption of elemental mercury from the Burger station sorbent.

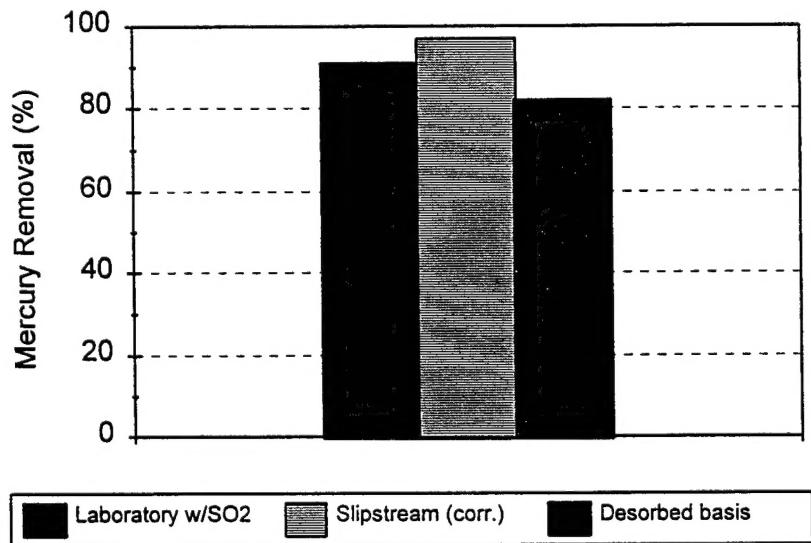


Figure 7. Elemental mercury removal in the laboratory, at the power plant and calculated from desorption.